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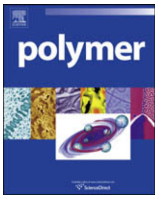

Feature Article

Uneven distribution of nanoparticles in immiscible fluids: Morphology development in polymer blends

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ABSTRACT

The present review aims at summarizing the current knowledge on how solid nanoparticles organize in polymer blends. First, the behavior of low viscosity fluid emulsions containing solid colloidal particles is briefly presented. By contrast with polymer blends, they have been the subject of intensive studies for a long time, with both applicative and comprehensive objectives. High viscosity fluid emulsions like polymer blends loaded with nanofillers have received less attention until the recent enthusiasm about nanotechnology and more specifically polymer nanocomposites. Some similarities and differences between both types of emulsions are highlighted. The solid particles are well known to distribute unevenly in those types of complex fluids and the factors that determine their distribution in polymer blends are discussed. A particular emphasis is given on the competition between thermodynamic wetting of the solid by the polymeric phases and kinetic control of the filler localization directly linked to the rate of the mixing process. This aspect is believed to be a specificity of filled polymer blends and is known to have a drastic and sometimes predominant effect on particle localization. It explains that finely tuned morphologies can be obtained where the particles do not occupy their equilibrium position.

1. Introduction

An emulsion is a mixture of two immiscible fluids in which one of the fluids is dispersed in the shape of droplets with a small size ranging from millimeters to less than 1 μm. This short definition is valid regardless of the viscosity of the liquids considered so that molten polymer blends may be considered as high viscosity fluid emulsions. With low viscosity liquid emulsions, the aim can be to obtain soft materials with special textures, tactile properties and flowing characteristics (stable liquid emulsions, foams, gels, flowing powders,…). Stable emulsions are also employed in the field of oil recovery, food industry, cosmetics. However, after homogenization, the immiscibility and incompatibility of the liquids may be the cause of macroscopic phase separation and depending on the application it is utmost important that this does not occur. One century ago, Ramsden [1] and Pickering [2] have noticed that not only surfactants are able to stabilize low viscosity fluids emulsions but that a small proportion of fine insoluble particles may be effective. Since then, several research teams have been studying emulsions containing particles like silica, carbon black, metal oxides or polymer latex. It has been clearly demonstrated that these colloids can adsorb strongly at the fluid-fluid interface and are consequently able to stabilize it. In the domain of high viscosity emulsions like immiscible polymer blends, the same conclusion was drawn but the causes of the morphology refinement and stabilization were less clearly ascertained. The first studies, in the sixties, concerned essentially elastomer blends with carbon black as the reinforcing filler [3,4]. At this time carbon black was not yet referred to as a “nanofiller” and carbon loaded rubbers as “nanocomposites” but both of them can be considered to be what is called now “nanomaterials”. Later, the studies were extended to thermoplastic blends [5]. In that context, carbon black was incorporated essentially to produce polymers with antistatic properties (conductivity) by taking advantage of an optimized state of aggregation and distribution of the filler through the concept of double percolation [6,7]. Recently, nanotechnology has become one of the most popular research topic and the investigations in the field of polymer matrix based nanocomposites occupy a large area

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in the scientific literature. The nanofillers have diversified, including spherical and aggregated silicas, nanoclays, micas, carbon nanotubes, polyhedral oligomeric silsesquioxane and others. These fillers have opened new perspectives since they vary by their shape factor (spheres, platelets, fibers), their surface energy and their ability to more or less disagglomerate or exfoliate depending on the mixing conditions and on the surface treatments applied [8].

At the present time, the influence of fillers on polymer blends' morphologies and on the stability of fluid-fluid emulsions is a matter of intensive investigations. However, the mechanisms by which particles inhibit coalescence are less completely understood in high viscosity polymers than in liquid emulsions that have been studied from the beginning of the 20th century. The latter topic has been reviewed by Tambe and Sharma [9] and more recently by Aveyard et al. [10] and Clegg [11] who presents the stabilization of bicontinuous gels by colloids and dedicates a section to polymeric fluids. In that context, the objective of the present review is to report and discuss current knowledge on the distribution of nanoparticles inside a binary polymer blend. As preliminary topic, in Section 2, the case of low molecular weight liquid emulsions containing colloids is briefly discussed with the perspective of better understanding the particularities encountered in viscous polymeric emulsions. Studies on filled polymer blends are presented in detail in Sections 3 and 4 with a particular emphasis given on the mechanisms of segregation of the solid particles in relation with the morphological specificities of such blends. Then, the different aspects of the stabilization are listed and although fundamental understanding of the phenomena is not totally gained, the important parameters are identified.

2. Low viscosity fluid emulsions

The main works in the field of stability and structure of emulsions stabilized by solid particles are those from Binks and co-workers. Different reviews have been addressed by these authors in the domain of particles at fluid-fluid interfaces [12] and on the preparation and properties of such stabilized emulsions [10]. More recently, Binks and Horozov [13] addressed a book to *Colloidal particles at liquid interfaces*.

2.1. Wettability

With the effect of the particle concentration and phase ratio, the influence of the wettability of the particles by the liquids is a first order parameter in the adsorption behavior of particles at the fluid-fluid interface.

At the equilibrium, the interfacial free energy, ΔG, of the interface should be minimum. ΔG may be expressed with the following equations if we consider the geometry depicted in Fig. 1 (Eq. (1)). It includes the contribution of three types of interfaces: solid/liquid 1, solid/liquid 2 and liquid 1/liquid 2.

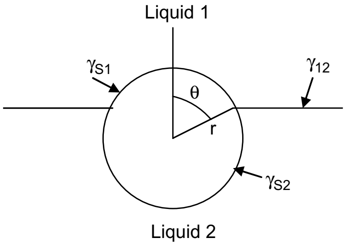

Fig. 1. Schematic representation of a spherical particle at the interface between liquids 1 and 2. Three types of interfaces are considered solid/liquid 1, solid/liquid 2 and liquid 1/liquid 2.

$$\begin{aligned}\Delta G &= \gamma_{S-1}\Delta A_{S-1} + \gamma_{S-2}\Delta A_{S-2} + \gamma_{1-2}\Delta A_{1-2}\\ \Delta G &= \gamma_{S-1}(2\pi r\sin\theta r\Delta\theta) - \gamma_{S-2}(2\pi r\sin\theta r\Delta\theta)\\ &\quad +\gamma_{1-2}(2\pi r\sin\theta r\Delta\theta)\cos\theta\\ \Delta G &= 0\end{aligned} \tag{1}$$

where r is the radius of the particle, γ_{S-i} is the interfacial tension between the particle and the liquid i, γ_{12} is the interfacial tension between the two liquids and A_{ij} is the area of the interfaces and θ is the contact angle (Fig. 1).

The interfacial energies can be used to express the wettability parameter, ω_{12}, according to Young's equation. It represents the ability of the particle to be wetted by liquids 1 and 2 and is directly linked to the contact angle θ defined in Fig. 2 for oil/water emulsion (1: water, 2: oil) (Eq. (2)):

$$\omega_{12} = \cos\theta = \frac{\gamma_{S-2} - \gamma_{S-1}}{\gamma_{12}} \tag{2}$$

The particles will accumulate at the interface provided that $|\omega_{12}| < 1$ as $0 < \theta < 180°$ which corresponds to $|\gamma_{S-2} - \gamma_{S-1}| < \gamma_{12}$. On the other hand if $|\omega_{12}| > 1$ that is $|\gamma_{S-2} - \gamma_{S-1}| > \gamma_{12}$ then solid particles will be localized in one of the two phases.

If the particle is hydrophilic, the contact angle θ (defined across the water) is slightly less than 90° ($0 < \theta < 90°$) thus the accumulation of a layer of particles closely packed at the interface promotes the formation of an interface curved toward the oil phase (Fig. 2). Consequently oil in water emulsion is obtained. If the particle is more hydrophobic, θ will be more than 90° ($90 < \theta < 180°$) and the curvature allows the formation of water in oil emulsion.

The free energy needed to remove the particles from the fluid interface is much greater than the thermal energy and is the highest for a contact angle equal to 90°. This feature explains that the particles can be viewed as irreversibly and strongly adsorbed (if the contact angle is not too far from 90°) by contrast with the classical surfactants which adsorb and desorb [12,14].

On the other hand, if the particles are too hydrophilic or too hydrophobic (θ too far from 90°), they will segregate in the water or in the oil phase resulting most often in poor stability. The structure of the interfacial particle layers is then governed by the balance of particle–fluid and particle–particle interactions.

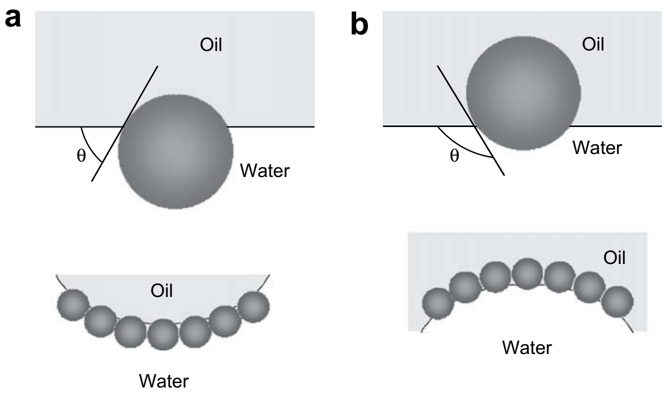

Fig. 2. Spherical particle at the oil/water interface. The contact angle, θ, is defined through the water phase. a) $\theta < 90$ °C: the particle is preferentially wetted by water. The particles are adsorbed at the interface so that oil in water emulsion is formed. b) $\theta > 90$ °C: the particle is preferentially wetted by oil. The particles are adsorbed at the curved interface so that water in oil emulsion is formed. From [12] reprinted with permission of Elsevier.

2.2. Aspects of emulsification

At the thermodynamic equilibrium, the formation of a particle layer at the fluid–fluid interface is therefore governed by the wettability of the particles. However, the emulsion formation is a dynamic process including two competitive processes: fragmentation of the liquid phase into smaller droplets and coalescence of these droplets resulting in large drops. Actually, the final morphology derives from the balance between drop breakup and coalescence. Generally speaking, this balance is governed by phase concentrations, interfacial tension and shear rate (more precisely capillary number), particle concentrations and time of emulsification. Binks and Whitby [15] investigated more precisely the influence of oil volume fraction, particle concentration and emulsification time on the stability of poly(dimethyl siloxane) (PDMS)/water emulsion in presence of hydrophobic monodisperse silica particles. As already reported in many works, the average drop diameter decreases with increasing particle concentration until a minimum size is reached. Furthermore, for concentration far away from phase inversion, the drop size decreases with mixing time as the breakup dominates during emulsification. Interestingly, coalescence becomes more dominant, i.e. the drop size increases with mixing time, for oil volume fraction close to conditions of phase inversion.

The mechanisms of the morphology stabilization in emulsions by solid particles is still an open discussion in the literature. As demonstrated by Okubo [16] and Vignati and Piazza [17], the interfacial tension between the two liquids of the emulsion is unaffected by particle adsorption. However, the area of the oil–water interface is reduced, which lowers the amount of energy required to form the interface. Therefore, a macroscopic or effective interfacial tension that should be lower than that of the oil–water interface in the absence of particles has been introduced by Levine and Bowen [18]. Actually, one of the mechanisms unanimously recognized by which coalescence is inhibited is that the particle dense layers at the interface act as a mechanical barrier preventing the rupture of the liquid film between two colliding drops under shear (Fig. 3).

It has been established that the mobility of the interface is one critical parameter influencing the drainage process. Indeed the rheological properties of the film which bounds the interfaces are of importance. Mobile interfacial layer allows faster film thinning while rigid interfaces slow down the process. In addition, film rupture requires that particles are removed from the drop–drop contact region and this can be achieved by two mechanisms: the displacement of the particles from the interface into the bulk phase (or to the dispersed phase) or the lateral displacement of particles along the interface. The latter requires much less energy than the former and thus is more likely to be the mechanism controlling the process. In this scheme, particle–particle interactions have a significant effect on the mechanical stability and strength of the solid layer since they render more difficult the lateral movements of the solid. The effectiveness of the barrier requires that the interface coverage is almost complete. However in some cases, only a partial coverage is required. When the particles are sufficiently mobile along the interface, they can move to the drop–drop contact zone and form a local dense monolayer that resist to coalescence but without needing total coverage of the drop (Fig. 4) [19–22]. Actually, this mechanism of bridging particles provides additional stability [23].

Finally, cases exist where stable emulsions can be obtained if high shape factor fillers are employed. Through their interactions they can form a three-dimensional solid network able to trap and immobilize the matrix (or the drops) and prevent drop coalescence [24].

To summarize briefly, the effectiveness of the emulsion stabilization is linked to the choice of particles with judiciously balanced wettability to ensure their placement at the interface. Furthermore, the particle size must be preferably less than 1 μm (and in any case significantly inferior to the diameter of the dispersed phase) and with a necessary degree of interparticle interaction. The amount of particles must be adjusted in order that they cover the interfacial area [25] for preventing drop coalescence by steric hindrance.

3. Partially miscible polymer blends filled with nanoparticles

Before taking up the topic of totally immiscible polymer blends, we will evoke the effect of nanoparticles in partially miscible polymer blends. Due to entropic effect disfavoring miscibility, polymers are most often immiscible. Although more rarely, some polymer pairs may exhibit partial miscibility either by cooling, for the systems with Lower Critical Solution Temperature (LCST), or by heating for the systems with Upper Critical Solution Temperature (UCST). The effect of fillers on the phase behavior of polymer pairs has been extensively studied and reviewed by the group of Lipatov [26–30]. Generally speaking, a change in the cloud point curves and phase compositions are reported due to the presence of nanofillers. The explanations for such behavior are not totally ascertained. It is proposed that the differences in phase separation of filled and unfilled mixtures can be linked to specific interactions and to preferential adsorption existing between the filler and one of the components of the blend. Experimentally, the estimation of the interaction parameter measured by inverse gas chromatography, has shown that its value may for instance decrease in the presence of filler. The authors propose that a border layer is formed whose composition differs from the bulk. In such a case, the system consists in regions with different polymer conformations and concentrations characterized by their own phase behavior, different from that on the unfilled system (Fig. 5). Upon phase separation, four phases will be formed: two phases at the interface and two in the bulk. This situation is valid only in the case of asymmetric interactions with the surface.

Another reason for changing the shape and position of the phase diagram is the possible selective adsorption of low (or high)

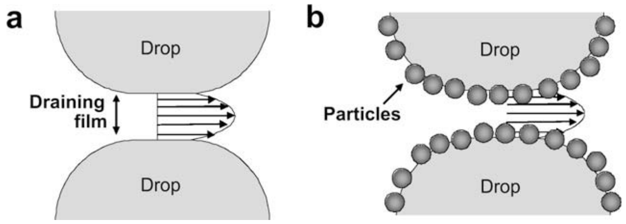

Fig. 3. Thinning of the film trapped between two liquid drops during their coalescence: a) free drops, b) drops covered by a layer of particles.

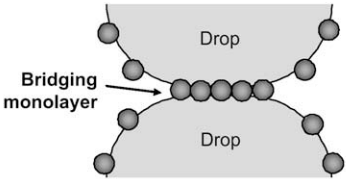

Fig. 4. Particles' monolayer bridging two drops during their approach is a possible mechanism for inhibiting coalescence without requiring a total coverage of the drop surface. From [21] reprinted with permission from John Wiley and sons.

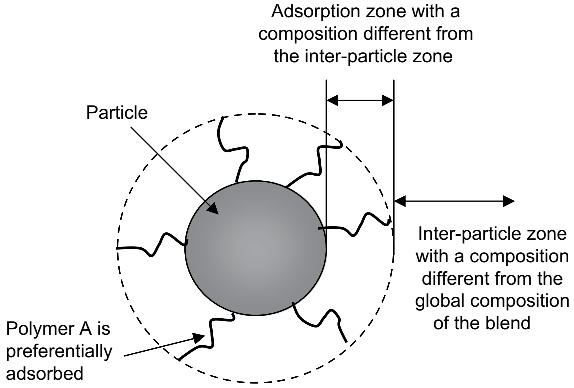

Fig. 5. Scheme of a filled partially miscible polymer blend in which one of the polymers preferentially interacts with the filler. The preferential adsorption of one of the polymers modifies the local composition and thus modifies the phase separation. The phase separating filled blend consists of phases whose compositions and structures depend on the respective interactions of both the polymer and the filler [30].

molecular weight fractions between the surface filler and the bulk which modifies the local molecular weight distribution.

As experimental examples of phase separation modification, Nesterov et al. observed that the LCST curve of poly(vinyl acetate)/poly(methyl methacrylate) (PVA/PMMA) mixtures were shifted to higher temperature, the miscibility window being enlarged in the presence of filler [27]. On the other hand, Lipatov et al. [28] found that introducing silica filler in chlorinated polyethylene/poly(ethylene-*co*-vinyl acetate) (EVA) blends led either to the increase or to the decrease in the temperature of phase separation depending on the filler concentration. Also, the phase separation temperature of a PMMA/poly(styrene-*co*-acrylonitrile) (SAN) blend [31] is increased and the thermodynamic interaction parameter is decreased due to the introduction of silica filler interacting preferentially with PMMA. With poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) miscible blend, the presence of carbon black was shown to induce spatial composition fluctuations due to the stronger interactions of PVDF with the filler [32]. The authors hypothesize that PVDF-rich regions are formed where the carbon black accumulates. The result in terms of conductivity was that carbon percolates at a lower concentration in the blend than in the pure polymers.

Moreover, the influence of strength of filler/polymer interactions has been highlighted experimentally by Karim et al. [33]. They found that the UCST curve of a polystyrene/polybutadiene blend is significantly altered by the addition of fumed silica. This alteration is dependent on the silica surface treatment. Actually, treated fumed silica (more hydrophobic) decreases the cloud point which corresponds to an enhancement of the blend miscibility (Fig. 6).

The fillers do not only modify the shape of the phase diagram, they also induce changes in the kinetics of phase separation [30]. The authors distinguish the case where a true thermodynamic equilibrium is reached to that where the reduced mobility of macromolecules adsorbed at the surface of the filler slows down the separation process. Indeed, most often phase separation is found to proceed slower in the presence of particles because of a reduction of macromolecular mobility. As an example, the fumed silica added in a polystyrene/poly(vinyl methyl ether) (PS/PVME) blend is segregating into the PVME-rich matrix during phase separation and acts as obstacle to the coarsening of the morphology [34].

Finally, fillers play a role on the morphology evolution during phase separation as was also reported for low viscosity emulsions [35]. The introduction of quantity as low as 0.8 wt% of three layered silicates differing by their lateral dimension in polystryrene/poly(vinyl methyl ether) (PS/PVME) films slows down the phase separation and also produces circular dispersed domains at a smaller length scale than the unfilled material [36].

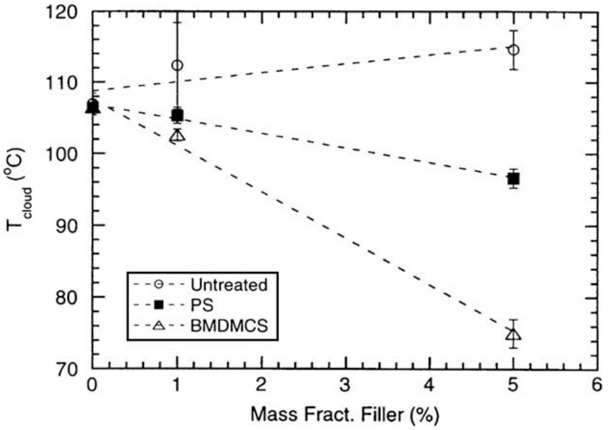

Fig. 6. Shift of cloud point temperatures of a polystyrene/polybutadiene 70/30 wt% with untreated and treated fumed silica. The symbols represent: (○) untreated silica, (■) polystyrene grafted silica, (△) bromomethyldimethylchlorosilane treated silica [33].

In the field of modeling, Ginzburg [37] formulated a theory to predict how nanoparticles interacting symmetrically with the polymers can influence the behavior of the blend. Depending on the particle radius and the polymer chain length, the presence of nanoparticles can either promote or hinder mixing of the polymers. Actually, the nanoparticles influence the shape and the location of the spinodal curve according to their size. If the radius of the nanoparticles is smaller than the radius of gyration of the macromolecule, the addition of the solid stabilizes the homogeneous phase because they reduce the number of unfavorable polymer/polymer interaction and therefore decreases the enthalpy of the blend. As the particle size becomes much larger than the polymer radius of gyration, the particle-rich phase segregates from the blend even at very low concentration. Then, nanoparticles can facilitate polymer blend miscibility provided that their sizes are lower than the polymer radius gyration, typically ∼15 nm. Furthermore, the high entropy of such small particles can also assist the free energy reduction and then the stability of the homogeneous phase. These findings have also been emphasized by the group of Balazs [38,39]. According to this model, Gharachorlou and Goharpey [34] showed by rheology, calorimetry and optical microscopy that the phase diagram of PS/PVME shifted up nearly by 10 °C in the presence of nanoparticles with the size comparable to the gyration radius of the polymers.

Hore and Laradji have simulated the effect of spherical particles which interact symmetrically with the two fluids (the condition $|\omega_{12}| < 1$ is fulfilled). Their central result is that particles migrate to the interface right after the induction of the phase separation process leading to a decrease of the domain growth kinetics. They found that the diameter of the particles was significant factor acting on the final domain size and on the separation kinetics. Smaller particles have a much higher probability to desorb from the interface thus producing larger domain size while particles with larger diameter remained at the interface leading to microphase separation [40].

4. High viscosity fluid emulsions: immiscible polymer blends

The comparison of low molecular weight fluid emulsions with polymer blends is not straightforward. In liquid emulsions, the distribution of particles corresponding to thermodynamic equilibrium can be attained after short times due to the weak resistance of low viscosity liquids (Stokes force) and their interface to particle movements. The issue associated with this short timescale is that demixing may be very rapid. Also, for applicative reasons, the stabilization of the emulsion has to be effective during very long timescale since emulsions are used as soft materials. As an example mayonnaise must retain its gel-like texture for weeks. By contrast, polymers are rarely used as liquids, they are used as solids with very low molecular mobility so that demixing of the phases during use cannot happen. There is a need for stabilization only when the blend is viscous (molten), that is during the mixing stage and during an eventual further processing. In other words, in polymers, the arrangement of the filler in one particular phase or at the interface is required either to obtain the desired property and/or to inhibit coalescence during the time needed for processing operations that is generally a few minutes. Molten polymers need to be stable during periods of time several orders of magnitude shorter than low viscosity fluid emulsions.

Adding solid particles in polymer blends is a traditional technique in rubber and thermoplastic processing. About 70% of polymer based materials contain solid particles, fillers of different size from few nanometers to micrometer. Originally, the purpose of adding particles in elastomer blends was obviously an applicative objective like obtaining high electrical conductivity or improving the mechanical properties. Since the typical size of the classical fillers (calcium carbonate, talc, silica) was of the same order of magnitude or greater than the size of the dispersed polymer phase, these particles were not found to interfere significantly with the blend morphology. The exceptions were the "old" nanosized fillers like carbon black or fumed silica. For instance, works on carbon black distribution in elastomer blends have been reported forty years ago [4,41,42]. These works were later extended to other elastomers and thermoplastic polymers mainly with the aim of minimizing the proportion of conductive fillers needed to induce electrical conductivity [32,43–57] and Huang [7] reviewed the works on the use of carbon black as conductive filler in polymer and polymer blends. Actually, the influence of fillers on blend morphologies has been reported far before the recent works on polymer nanocomposites and the idea of compatibilizing a blend by using inorganic particle.

From material development point of view, a requisite is to predict how additives will affect the performances of the material, and undoubtedly the way these additives distribute inside the material is of crucial importance. Thus, similar to fluid emulsions, a challenge in formulating polymer blend nanocomposites is to control the blend morphology that is not only the shape and size of the dispersed polymer domains and their interfacial interactions with the matrix, but also the state of dispersion and the distribution of the fillers. It requires having identified and classified the mechanisms involved in the particle movements and localization inside the material if one aims at obtaining tailored morphologies.

4.1. *Interactions in filled polymer blends*

Compared to liquid emulsions, polymer blends differ not only by their high viscosity but also by their lower interfacial tension. Water is often more polar than a polymer so that interaction forces of particles at the interface of molten polymers are weaker than those in water–oil emulsions. This feature implies that the physical interaction forces exerted at the surface of the filler will be smaller than that encountered in water liquid emulsions (if we don't take into account that polymer chains may be strongly adsorbed or even covalently grafted at the filler surface).

As for liquid emulsions, the localization of nanoparticles in polymer blends should be linked to the balance of interactions between the surface of the particles and the polymer components as was qualitatively highlighted in earlier studies dealing with the use of carbon black in elastomer blends. As a consequence, in the overwhelming majority of systems, the nanofillers distribute unequally between the polymer phases. Uneven particle distribution depends on the balance of interfacial energies and can be predicted by calculating the wetting parameter, ω_{12}, defined previously in Eq. (2). Two cases exist: when $\omega_{12} > 1$ the particles are present only in polymer 1, for value of $\omega_{12} < -1$ they are only found in polymer 2 and for other values of ω_1, $(-1 < \omega_{12} < 1)$ the particles are concentrated at the interface between the two polymers. The third situation corresponds to $|\gamma_{S-2} - \gamma_{S-1}| < \gamma_{12}$ which is more likely to occur in polymer blends with a high degree of incompatibility or when the differences in the filler/polymer interactions are small.

In principle the knowledge of the polymer/polymer and of the polymer/filler interfacial tensions should be sufficient to anticipate the morphology. However, if experimental data may be found for polymer/polymer interface it is almost impossible to find it for polymer/filler. Usually, they are estimated with the help of theoretical models like the well-known Owens–Wendt [58], Girifalco–Good [59,60] or Wu equations [61] (Eqs. (3)–(5)):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}} - 2\sqrt{\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}} \tag{3}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2} \tag{4}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1\gamma_2}{\gamma_1 + \gamma_2} \tag{5}$$

Only γ_i, the surface tension of component *i* needs to be known. The exponents d and p stand for respectively the dispersive and the polar contribution to the surface tension. Such calculations, from Owens–Wendt equation, have been performed by Sumita and co-workers for polyethylene/polypropylene (PE/PP), polyethylene/poly(methyl methacrylate) and polypropylene/poly(methyl methacrylate) blends filled with carbon black [5,62]; by Ibarra-Gomez for polybutadiene/poly(ethylene-*co*-propylene-*co*-diene monomer) (BR/EPDM) blends filled with carbon black [63]; by Katada and co-workers for EVA/poly(L-lactic acid) (PLA)/carbon black [54] and by Elias et al. for silica particles dispersed in PP/PS and PP/EVA blends [64,65]. At this stage it is important to point out that these authors calculated the surface tension at room temperature and that the melt surface tension of polymers can be different from solid surface tension. Actually, the value at high temperature is the relevant data that should be inserted in the thermodynamic model (mixing is done at $T > 150\,^{\circ}\mathrm{C}$). Elias et al. corrected their data with the help of the expression proposed by Guggenheim [84] but this is rarely done.

Tables 1 and 2 present the calculation of surface energies and of the wetting parameter at room temperature using Girifalco–Good and Wu equations. Even some discrepancies between the predictions of these equations are significant, the localization of the fillers was correctly predicted in a number of studies. Note that qualitative works have also analyzed filler localization in polymer blends loaded with different types of nanofillers [66–72]. Their observation of the filler distribution was only based on the measurement of the electrical conductivity (carbon black filler) or the mechanical properties of the blends.

The approach of Zaikin et al. to predict the filler distribution is original and interesting [72,55]. The authors have blended a number of different polymers one with the others with carbon black. In order to evaluate the affinity of the polymers with the fillers, which is not possible since it does not exist easy and reliable technique, they have selected low molecular weight liquids analogs

Table 1
Surface energies of some polymers and fillers.

	γ	γ^d (mN/m)	γ^p (mN/m)
Polymers			
PE[a]	25.9	25.9	0
PP[a]	20.2	19.8	0.4
PP[b]	30.1	30.1	0
PMMA[a]	28.1	20.2	7.9
PS[b]	40.7	30.5	6.1
EVA 28[b]	35.9	33.4	2.51
EVA 39[c]	25.9	23.1	2.8
PLA[c]	34.8	17.5	17.3
Fillers			
Carbon black[a]	55	51–49	4–6
Carbon black[c]	108.1	108.1	0.7
Hydrophilic silica[b]	80	29.4	50.6
Hydrophobic silica[b]	32	30	2

γ^d, γ^p: dispersive and polar components; EVA 28 and 39 contain respectively 28 and 38% of vinyl acetate units.
[a] Values from Refs. [73] and [5].
[b] Values from [64].
[c] Values from [54].

of the polymers. As an example, hexane was employed to estimate polyethylene/carbon interaction. The enthalpy of wetting of the filler by the liquids was measured and gave an indication on the interaction energy. In addition, they estimated the bonding strength between the filler and polymer by measuring the increment of the peeling force exerted between a layer of the studied polymer and a layer of PP when its carbon black content increased from 0 to 42 vol%. Their results are summarized in Table 3. These data permit to classify the polymers with respect to their interaction with the filler. Also, it is noticeable that the force of peeling of the polymers qualitatively correlates with the estimation of the interactions of the liquid analogs with the filler. The approach allowed the authors to bring qualitative interpretations for the distribution of the carbon black in their blends.

Another interesting attempt to quantify the interactions and relate them to the distribution of the particles is that of Thareja and Velankar [74]. They studied two blends with more or less chemical differences between the two polymers. Polyisoprene/poly(dimethylsiloxane) (PI/PDMS) had more chemical difference than polyisoprene/polyisobutylene (PI/PIB) (Table 4). They used the Girifalco–Good theory and assimilated the surface energies needed in the model to the critical surface tension of the particles estimated by a float or sink test. The equation allowed to determine for which range of surface tension the filler will show interfacial activity. Theoretically only the poly(tetrafluoroethylene) (PTFE) filler should locate at the interface however, experimentally all types of fillers where observed at the PI drops surface (Table 4). No definitive explanation of the disagreement between theory and experiments was proposed but the authors point out that the approach to derive interfacial tension from surface tension may be too simplistic. Other theories exist but require data that are difficult to obtain experimentally.

It was shown above that the attempts to predict the preferred arrangement of the fillers inside a polymer blend are sometimes useless and several studies reveal that the knowledge of the wetting parameter or the estimation of the interactions are not sufficient to determine where the filler will be located. Actually, a first problem is the quantitative determination of the surface tension of the different components (polymers and filler) especially at high temperature. Some strong discrepancies are reported for the surface tensions. Furthermore, it can be pointed out that most of these systems are based on commercial products which then contained some additives (stabilizers mainly). These additives, even at low concentration, can considerably alter the surface tensions of polymers. A second point is that strong and preferential

Table 2
Wetting parameter ω_{12} for different blends/fillers. The filler localization was characterized by electron micoscopy.

Polymer 1	Polymer 2	Filler	ω_{12}	ω_{12}	ω_{12}	Filler localization
			Owens–Wendt	Girifalco–Good	Wu	
PMMA	PP	Carbon black	0.75–0.31[a]	−19.63	−10.24	Interface
PMMA	PE	Carbon black	−0.1 to 0.28[a]	−20.98	−19.63	Interface
PE	PP	Carbon black	3.5–3.75[a]	−8.82	−8	PE phase
PS	PP	Hydrophilic silica	4.87[b]	−6.74	−6.18	PS phase
PS	PP	Hydrophobic Silica	−1.13[b]	0.62	0.62	Interface
EVA	PP	Hydrophilic silica	8[b]	12.63	11.4	EVA phase
EVA	PP	Hydrophobic silica	0.72[b]	−0.33	−0.33	Interface
BR	EPDM	Carbon black	5.15[c]			BR phase
EVA	PLA	Carbon black	2.69[d]	94.2	80	EVA phase

[a] From [5].
[b] From [64].
[c] From [63].
[d] Values from [54].

Table 3
Characterization of the interactions of polymers and their low molecular weight analogs with carbon black [55].

Polymer	ΔF (kN m^{-1})	Low molecular weight analog	ΔH (mJ m^{-2})
Polyethylene (PE)	0.025	*n*-Hexane	170
Polyisobutylene (PIB)	0.02	2,2,4-Trimethylpentane	175
Polystyrene (PS)	0.015	Ethylbenzene	205
Poly(ethylene-propylene-diene) (EPDM)	0.15	1-Hexene	180
Polydimethylsiloxane (PDMS)	0.03	Octamethylcyclotetrasiloxane	200
Poly(ethylene-*co*-vinyl acetate) EVA	0.3		
Nitrile–butadiene rubber (NBR)	0.46		
Poly(chloroprene) (PCP)	0.65	1-Chlorobutane	270
Polyurethane (PU)	1.17		
Polyvinyl alcool (PVA)	2	Ethyl acetate	365

ΔF is the increment in the strength of polymer peeling off a PP plate with a carbon black content increased from 0 to 42 vol%. ΔH is the enthalpy of wetting of the carbon black by the liquids.
PU is made from polyoxytetraethylene glycol, 4,4-diphenylmethane diisocyanate, and 1,4-butanediol.

Table 4
Polymer, and filler surface tensions. Polymer blend interfacial tensions and conditions for the localization of the fillers at the interface of the two blends estimated with the Girifalco–Good model [74].

Polymers	Surface tension (mN/m)	Interfacial tension of the blends (mN/m)
PDMS	19.2	PI/PDMS $\gamma_{12} = 2.73$
PIB	32.1	PI/PIB $\gamma_{12} = 0.28$
PI	35.9	

	Fillers				
	PTFE	Hydrophobic silica	TiO_2	FeOOH	Fe
γ_S estimated by float/sink test (mN/m)	25–28.5	38.8–43.9	50.8–63.3	63.3–72.3	Uncertain, 46 for pure Fe

Limits in γ_S for particles localization at the interface	In PI/PDMS	$18.8 < \gamma_S$ (mN/m) < 36.4
	In PI/PIB	$29.1 < \gamma_S$ (mN/m) < 39.2

interactions can be created at the filler/polymer interface through adsorption of the polymer chains or their covalent grafting or also macromolecules intercalation in between clay platelets. Finally, it must be emphasized that the localization of particles is determined by the thermodynamics of wetting only provided that thermodynamic equilibrium is attained. This implies that the processing conditions have to be carefully considered and kinetic effects induced by mixing procedure and mixing time have definitely to be taken into account.

4.2. Kinetic effects

Kinetic effects are linked to the rate of the mixing process. When two polymers are blended with a filler the final equilibrium morphology (shape and size of the polymeric phases), the state of dispersion of the filler and its distribution inside the blend are not immediately attained because of the high viscosity. Several factors can influence the rate of establishment of such equilibrium.

4.2.1. Mixing procedure

The order of addition of the components is of importance and can have a strong effect on the kinetics and intensity of mixing because it has a direct influence on the medium with which the filler will be in contact during the course of its incorporation. By "medium" we mean the nature of the polymer in contact and its state of melting. The simplest procedure and the most reported in the literature is the addition the components all together in the mixer. They are blended at a temperature high enough to ensure that the polymers will transform into viscous fluids, however a stage where the materials are solid and then progressively melted precedes the actual melt blending. The process is complex, involving mixtures of solids and viscous fluids and the simultaneous evolution of the morphology of the polymer blend together with the dispersion and migration of the particles inside the molten material. With this first mixing procedure, if one polymer melts at a temperature significantly lower than the other (melts first), the solid particles may be incorporated into it preferentially although the said polymer does not have the better affinity. Since the obtained initial distribution will not be that corresponding to the thermodynamic equilibrium, different scenarios are then possible where the filler will have or not the opportunity to migrate to the preferred phase or to the interface. A second alternative consists in melting the two polymers and afterward adding the filler so that the particles do not see any solid medium. Thirdly, it is possible to incorporate the filler into the first polymer and then introduce the second polymer. Depending on these sequences of addition of the components, the filler may also have to transfer from one phase to the other to reach its equilibrium distribution and this involves particle displacement inside the blend. The easiest way to highlight the existence of particle movement inside a blend is to incorporate the solid particles in the polymer having the lower affinity and then to add the higher affinity polymer. This phenomenon has been discussed in the case of elastomer blends filled with carbon black [4,41,42]. These systems contained vulcanization additives and oil which do not facilitate the interpretation however the impact of the degree of saturation of the elastomers was found to influence the carbon black partition. Zaikin et al. have varied the sequence of mixing of their polymer pairs with carbon black showing enhanced conductivity when the filler had to cross the interface [55,72]. Elias et al. have selected a PP/PS/silica blend and a sequence of addition where the silica was first mixed with PP and this composite was then mixed with PS [64]. They observed that all the hydrophilic silica transfers from the PP with which it has lower affinity toward the PS preferred phase where it concentrated (Fig. 7). A few minutes mixing were sufficient for the transfer to occur.

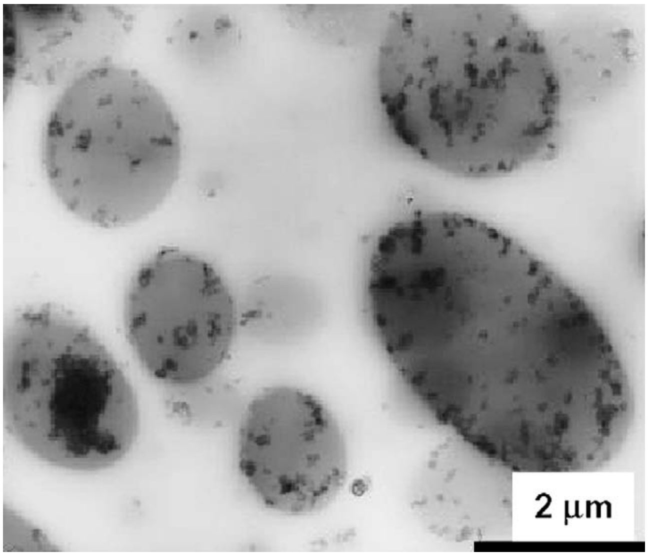

Fig. 7. Micrograph of PP/PS 70/30 wt% containing 3 wt% hydrophilic silica. The nanocomposite was obtained by premixing the silica with PP before adding the PS. The silica particles have totally migrated from the PP matrix to the PS phase which has better affinity with this filler. The dispersed PS phase appears in grey and the silica in black [64].

Another example is presented in a series of papers by Gubbels et al. [75,44,45] that introduced carbon black in polystyrene/polyethylene to obtain electrical conductivity. These studies, although not the more recent, illustrate well some of the factors involved in the distribution of nanofillers in polymer blends and how they can influence on the material properties. The authors first emphasize that the localization of the filler has a tremendous influence on the value of the percolation threshold needed to observe a significant conductivity of the material. They compare four situations where the filler is dispersed: 1) in an amorphous polymer (PS), 2) in a semi-crystalline polymer (PE), 3) in a PS/PE 45/55 blend where the carbon is confined inside the PE phase and 4) in the same PS/PE blend but with the carbon localized at the interface. The second situation is better than the first thanks to a segregation of the carbon black during the crystallization of the PE. Situation 3 is again better because a double percolation is created: percolation of the PE phase by adequately tuning the proportion of the phases and percolation of the carbon black inside the PE is observed at the concentration close to 3 wt% (Table 5). Note that the percolation threshold of carbon black homogeneously dispersed in a polymer matrix is close to 20 wt%. As proved by TEM images, the carbon particles are confined at the interface in a two-dimensional space. Note that this concept of multiple percolation has been first introduced by Sumita et al. [6] and Levon et al. [76]. Such co-continuous system with the carbon at the interface can be produced by compression molding PE and PS powder together with the filler. But more interestingly it can be produced by taking advantage of the possible migration of filler from the less interacting phase (PS) toward the more favorably interacting one (PE). In practice, carbon black has been first mixed with the molten PS and then PE is added. Here, kinetic effects are illustrated clearly: as the mixing time increases, the carbon particles will show the tendency

Table 5
Percolation threshold of carbon black in three different composites [75].

Carbon black dispersed	Percolation threshold (wt%)
In PE matrix	5
In the PE phase of a 45/55 PE/PS blend	3
At the interface of a 45/55 PE/PS blend	0.4

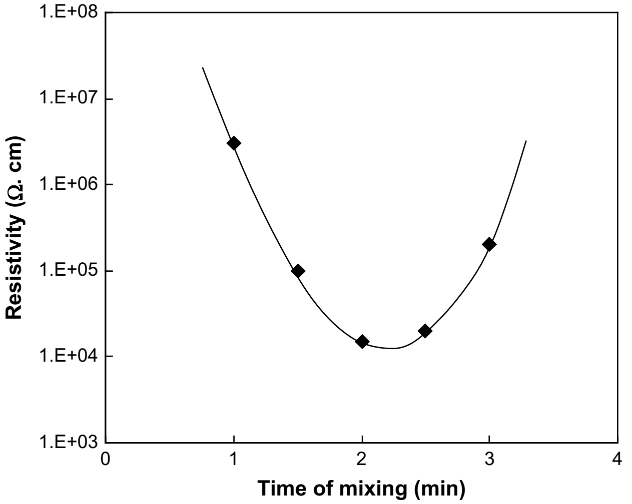

Fig. 8. Electrical resistivity versus mixing time of PE/PS co-continuous (45/55) blend filled with 1 wt% of carbon black. From left to right CB is localized in the PS phase, then at the interface (minimum of the resistivity) and finally in the PE phase. From [75] reprinted with permission from ACS: Macromolecules.

to transfer from one phase to the other by crossing the interface. The resistivity passes through a minimum when the particles have accumulated at the interface, then resistivity progressively increases when the carbon leaves the interface to concentrate into the PE phase (Fig. 8). If mixing is stopped at the adequate time, the particles will remain at the interface upon cooling the blend whose morphology is then quenched at a non-equilibrium state (Fig. 9).

With this strategy only 0.4 wt% of carbon in a PE/PS 45/55 was enough to obtain conductive of the material with a resistivity close to 100 Ω cm.

To summarize, the approach described above consists in driving particles to the interface by transferring them from one phase to the preferentially interacting one and taking advantage of the temporary state where they are blocked and accumulate at the interface (kinetic control). On the other hand, if the surface affinity of the particles is balanced with that of the two polymers by modifying chemically the filler surface, they will thermodynamically be stabilized at the interface regardless of the mixing time (thermodynamic control) [45]. Thus if a specific particle localization is desired, expensive filler surface treatments may be avoided by taking advantage of the kinetic control of the morphology.

It can be pointed out that carbon black is a very interesting filler to study since the electrical properties of the blends will provide information on its morphology (percolation of the phases) and also on the position of the carbon particles and their degree of agglomeration. Also, the surface of carbon black may be easily treated in order to modify its polarity. Nevertheless, one aspect complicates the situation: the state of agglomeration of carbon black and thus the percolation threshold may be altered depending on the nature and viscosity of the polymer phase in which it is dispersing. As a consequence it is not always straightforward to draw conclusions by considering only the electrical conductivity measurements.

Carbon nanotubes have also been considered to be attractive fillers for improving the electrical conductivity of polymeric blend materials. The concept of double percolation has been tested on several types of blends. The filler was found to concentrate inside the more polar phase, polycarbonate [77,78], poly(ethylene terephthalate) [79] or polyamide [80]. An interesting issue may be: are such high shape factor fibrous nanoparticles able to transport from one phase to the other? Unfortunately, the mode of addition of the nanotubes in the more favorable phase first did not permit to bring an answer to this question.

4.2.2. *Viscosity*

In viscous medium like polymer melts where the flow is laminar, the kinetic effects are directly related to the shear viscosity of the phases nevertheless its influence on the particles localization is rarely studied systematically. The literature on low viscosity emulsions does not highlight this point since kinetic effects are less likely to occur. Gubbels et al. [45] propose that the transfer of filler from one phase to the other is slower when the particles are originally confined in the more viscous phase but in their system the difference in behavior may also be attributed to some difference in the thermodynamic interactions so it is difficult to conclude. The effect of viscosity is highlighted by Ibarra-Gomez et al. on their rubber blend but no critical analysis of this effect is proposed [63]. In the study of Persson and Bertilsson, polyethylene/polyisobutylene (PE/PIB) blends with different viscosity grades are filled with aluminium borate whiskers with a rather complex blending sequence [81]. These whiskers are not exactly of nanoscale but this work is interesting in the sense that it comments about the relative importance of interaction strength and viscosity effects. The whiskers have high energy surface while the PE/PIB interfacial tension is low. The interaction difference is rather small although PE should interact slightly more with the filler than the PIB. Their first observation is that the whiskers accumulate in the more viscous phase because the blend organizes itself to minimize its dissipative energy during mixing. They support their hypothesis by estimating (with the help of theoretical models) the viscosities of the filled blends making the assumption of filler repartition in one polymer or the other. Finally they compare the PE/PIB blend with a polyamide/poly(styrene-*co*-acrylonitrile) (PA/SAN) and observe that all the whisker particles reside in the PA phase although it is less viscous. This result is contradictory with their conclusions on

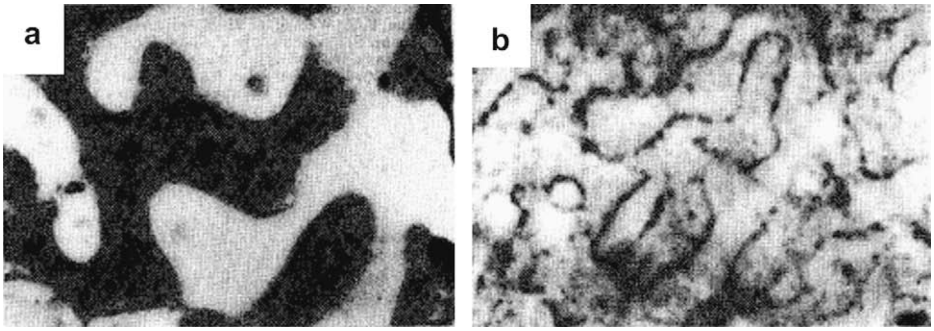

Fig. 9. Optical micrographs of a PE/PS 45/55 blend filled with 1 wt% of carbon black. a) Carbon black localized in the PE phase, b) carbon black localized at the interface by taking advantage of the transfer of the filler from the PS phase toward the PE phase. From [75] reprinted with permission from ACS: Macromolecules.

the effect of viscosity. They hypothesize that viscous distribution effects are weak and dominate only when the difference of interactions between polymer A/filler and polymer B/filler is small. By contrast when one of the polymers interacts much more favorably than the other with the filler (PA in the PA/SAN blend) then the thermodynamic interactions will dominate the viscosity effect. These comments illustrate the difficulty encountered to decouple the effects of thermodynamic wetting from kinetic effects. In that sense, the work of Feng et al. with PP/PMMA/carbon black blends is particularly interesting because the authors use three types of PMMA with different molecular weights while PP does not change [82]. Accordingly, the effect of the viscosity ratio is investigated. The calculation of the wetting parameter predicts that carbon particles should be dispersed in the PMMA phase. The three components are added at the same time in the mixer and PMMA is the minor phase. The TEM observations demonstrate that the confinement of carbon black into the PMMA phase is attained only with the blend with viscosity ratio close to 1 (Table 6).

In the situations where PMMA is more viscous than the matrix, the particles remain at the interface (for the medium viscosity PMMA) or in the PP phase (for the highest viscosity PMMA). Their results disagree with those of Persson and Bertilsson presented before but agrees with Clarke et al. [83]. More recently, the work of Elias et al. concerns two types of fumed silica with different hydrophilicities in PP/EVA 80/20 wt% blends [84]. The viscosity of the EVA samples is varied with a very fluid EVA (EVA-2, $\eta_0 = 12$ Pa s) and a grade with a viscosity close to that of PP (PP: $\eta_0 = 2500$ Pa s and EVA-1: $\eta_0 = 3100$ Pa s). The morphologies obtained are depicted in Fig. 10. The wetting parameters predict that the hydrophobic silica should localize at the interface while the hydrophilic should distribute in the EVA.

Indeed Fig. 10a and b shows that the hydrophilic silica particles distribute in the EVA regardless of the EVA viscosity. On the other hand hydrophobic silica reaches completely the interface only in the case of the low viscosity EVA (Fig. 10c and d). It is necessary to consider that the three components are added at the same time in the extruder and that EVA is melted before PP (~70 °C compared to 165 °C for PP) so that the silica is probably incorporated in EVA at the early stages of the mixing process. Yet, hydrophilic particles simply remain in their preferred phase. Besides, hydrophobic particles have to move from the inside of the EVA domains toward their surface to attain their equilibrium position and this migration is found to be easier when the EVA domains are less viscous. The viscosity effect was also reported by Clarke et al. [83] and Zhou et al. [85] for carbon black particles. They showed that under normal processing conditions carbon black particles tend to be preferentially incorporated into the lower viscosity polymer. They also finally argued that the interfacial energy of particle–polymer can be considered as the dominant factor only when the viscosity ratio of both polymer phases is nearly one.

Table 6

Localization by TEM observation of the fillers in PP/PMMA blends [82] and PP/EVA [84] blends where PMMA and EVA are the dispersed phase respectively. All components were added all together in the mixer.

Blends	Localization of the filler
PP/PMMA-1	Carbon black in the PMMA phase
PP/PMMA-2	Carbon black at the interface and in the PP
PP/PMMA-3	Carbon black the PP phase
PP/EVA-1	Hydrophilic silica in EVA phase (Fig. 10a)
PP/EVA-2	Hydrophilic silica in EVA phase (Fig. 10b)
PP/EVA-1	Hydrophobic silica in EVA phase (Fig. 10c)
PP/EVA-2	Hydrophobic silica at the interface (Fig. 10d)

PP/PMMA blends: the viscosities of the PMMA are classified as follows: PMMA-3 ($M_w = 350{,}000$ g mol^{-1}) > PMMA-2 ($M_w = 82{,}700$ g mol^{-1}) > PMMA-1 ($M_w = 25{,}000$ g mol^{-1}). PP has a viscosity close to that of PMMA-1.

PP/EVA blends: the viscosities of PP, EVA-1 and EVA-2 are 2500, 3100 and 12 Pa s respectively.

The above results illustrate the fact that viscosity can play a dominant role but descriptive interpretations are difficult to propose. Several reasons may be put forward. Actually, it is a real issue to disconnect viscosity effects from the other influent phenomena like thermodynamic interactions and kinetic effects. Mixing is a dynamic process during which two polymers are molten (sometimes at different temperatures), the morphology evolves and in addition fillers are displacing and dispersing in the respective phases and at the interface. The local and temporal variations of viscosity are huge rendering the analysis almost impossible unless model conditions and blends are selected. This picture of the problem is complicated by the fact that the observations of the blend morphology should ideally be made all along the mixing process and not only after a given time. To be even more particular, one must not forget that the state of agglomeration (or exfoliation) of the filler is an additional (and evolutive) parameter that should also be considered and quantified since it can alter drastically the viscosity of the phases and the mobility of the blend interface.

4.2.3. *Mechanisms of particle migration*

If the role of interfacial interactions on particles localization is abundantly discussed in the literature, the way by which nanoparticles transfer from one phase to the other, passes the interface or more generally moves inside the blend at the molten state are almost never mentioned. In other words, the experimental observations evidence the migration of particles in polymer blends but the fundamental processes by which this migration occurs are not discussed.

Elias et al. have listed and discussed at least qualitatively these mechanisms [84]. The uneven distribution of particles and their migration from one phase to the other implies first that the particle approaches the interface. Three mechanisms can be involved:

- The first one is the Brownian motion of the particles (self-diffusion of the particles). The diffusion coefficient D_0 of a spherical particle of radius a in a fluid with η_S viscosity at temperature T can be expressed as:

$$D_0 = \frac{k_B T}{6\pi \eta_S a} \tag{6}$$

Where k_B is the Boltzmann constant.

Consequently, the time t_D for a particle to diffuse on a distance equal to its radius, a, is equal to:

$$t_D = \frac{a^2}{D_0} = \frac{6\pi \eta a^3}{k_B T} \tag{7}$$

If we assume that the characteristic size of diffusing particle aggregates is $a \approx 100$ nm, we find that $t_D \approx 7500$ s for $\eta = 2.5.10^3$ Pa s (PP viscosity) and $T = 473$ K. This rough calculation shows that the order of magnitude of the motion time is very large and consequently not compatible with the mixing time which is equal to a few minutes. Generally speaking, the high viscosity of the molten polymer impedes the particle movement by Brownian motion. Thus, the migration of particles cannot occur under static conditions in molten polymer. By contrast, the time of diffusion in liquid emulsion will be of the order of magnitude of milliseconds. The time of diffusion from one phase to the interface (distance of few μm) will be then of few seconds.

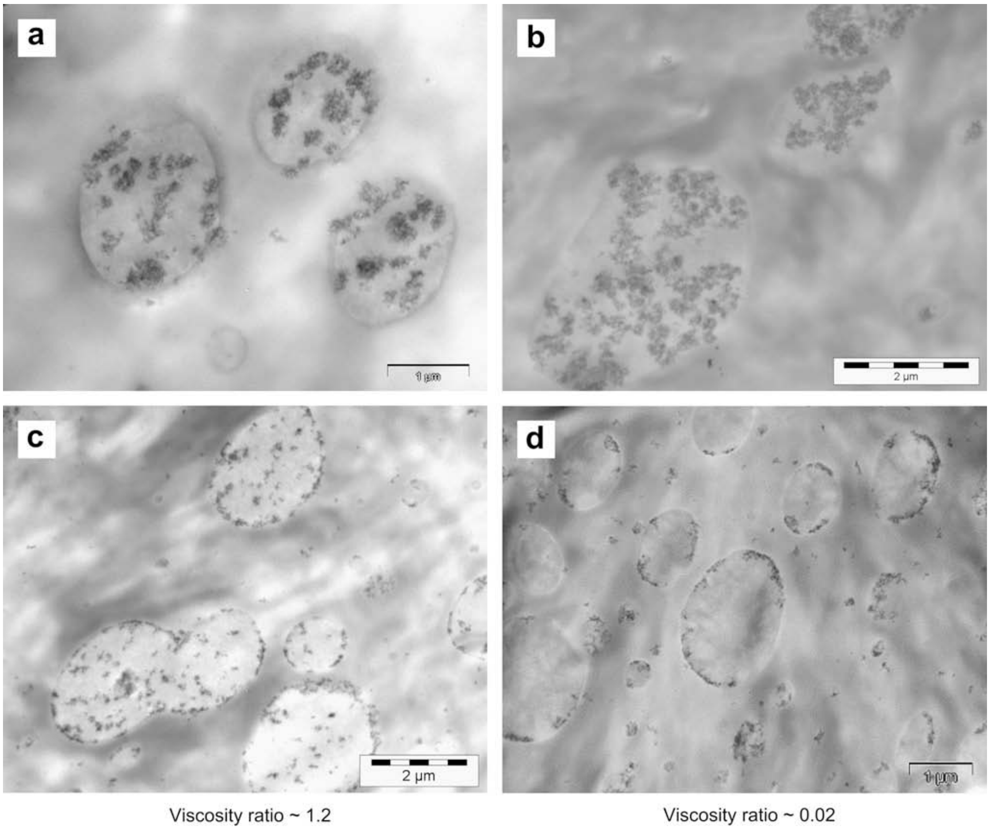

Fig. 10. TEM images of PP/EVA/silica (87.6/19.4/3 wt%). (a) PP/EVA-1/hydrophilic silica, (b) PP/EVA-2/hydrophilic silica, (c) PP/EVA-1/hydrophobic silica, (d) PP/EVA-2/hydrophobic silica. The polymer components and silica particles were added simultaneously in the extruder. $p = \eta_{EVA}/\eta_{PP} = 1.2$ for EVA-1 and $p = \eta_{EVA}/\eta_{PP} = 0.02$ for EVA-2 (at shear rate - = 100 s^{-1}). From [84] reprinted with permission from John Wiley and sons.

- The second possibility is the particle movement induced by the shear. Actually, the inorganic particles and the droplets of the dispersed phase are moving into the matrix so that collisions between particles and drops occur. The frequency of collisions may be roughly approximated by the following equation [86,87]:

$$C = \frac{8}{\pi}\dot{\gamma}\Phi \tag{8}$$

Φ is the volume fraction of the considered dispersed entity (particle or polymer drops). If we consider that the shear rate is equal to 100 s^{-1} and that $\Phi \approx 1.5$ vol% (in the case of the solid), then $C \approx 4$ collisions per second. If we take $\Phi \approx 20$ vol% (in the case of the polymer drops), then $C \approx 50\ s^{-1}$. These values illustrate the fact that particles are subjected to numerous collisions with the drops. These collisions may or may not end up with the embedding of a particle into the dispersed domains. Nevertheless, it must be noticed that solid particles are very small and rigid entities so that the drainage of the polymer matrix film trapped between the drop and the particle should be greatly facilitated compared to that involved when two dispersed polymer drops are colliding [88] or when a large particle and a drop are colliding [89]. Thus, this contribution is most likely to be a dominant one.

A second situation exists where the filler is embedded in the drops and tends to move toward the matrix. It is almost never discussed in the literature. The migration of particles from the matrix to the drops is more easily intuited but evidence exists that it is not the only possible migration type. The experiments of Elias et al. have demonstrated that the transfer of a silica particle from a drop to the matrix was possible and proceeded rapidly [84]. Austin and Kontopoulou observed that nanoclay migrates from the PP drops toward the maleated poly(ethylene-*co*-propylene) matrix [90]. These features show that the velocity field inside the drop causes the solid particles to move, possibly cross the interface and eventually be transferred to the matrix by a mechanism very similar to the particle–drop collision.

- A third mechanism could be proposed where particles are trapped in the inter-droplet zone during a collision between two dispersed polymer drops. In this latter case, it is the coalescence of polymer droplets that is playing a role in the transfer of the solid from one phase to the other. It is difficult to declare whether this latter mechanism is significant or not since to our knowledge no literature may be found on such phenomenon. Its efficiency should depend a lot on the size and deformability of the drops. Highly deformable drops are being probably able to trap more easily the solid particles in the interface. Nevertheless in polymeric emulsions the frequency of collision of polymer drops is very high so that the contribution of this mechanism must be kept in mind.

The above comments are related to particle movements inside the molten heterogeneous medium. Besides, surface effects must be considered. When the particles transfer from one phase to the other, they have to cross the interface which implies that the macromolecules adsorbed on the filler surface must desorb progressively to be replaced by the other polymer (the one with the better affinity). If the energy barrier for desorption is high, this process may not be immediate so that particles will reside at the interface for a certain period of time [55]. The competitive adsorption of polymer blends' melts on solid particles is rarely studied in contrast with polymer solutions but is must be considered when trying to draw a global description of the process because this step may possibly be the one limiting the transfer [91–93]. This aspect is complicated by the possible modification of the surface tension of the polymer at a few nanometers length scale by the presence of a high energy substrate (here the filler) [94]. Finally, although this point is never discussed in the literature, we can imagine that during mixing high shear forces are able to shift the adsorption/desorption equilibrium by extracting the particles from the interface.

4.3. *Compatibilization of immiscible polymer blends*

It is well known for years now that the compatibilization of immiscible polymer blends is most often achieved by adding block copolymers (or by in situ synthesis of this copolymer) that play a role similar to emulsifiers in liquid emulsions [95]. The localization of the copolymer at the interface inhibits coalescence and results in a fine morphology that is besides stable toward further processing step. Also very important is the fact that interfacial adhesion is enhanced, allowing to obtain good ultimate mechanical properties that by contrast are known to be particularly bad in non-compatibilized blends. To summarize, what is expected from an efficient compatibilization is the reduction of the characteristic size of the polymer domains, their stabilization against processing or annealing and good mechanical properties.

4.3.1. *Morphology changes*

The information found in the literature on the effect of the filler on morphology is clear: a decrease of the size of the dispersed polymer domains is reported in elastomers and in thermoplastic polymers. Coarsening is sometimes observed, for instance by Gahleitner et al., but difficult to interpret since the PA/PP blend of their study contained also functional polymeric compatibilizers and mixing sequences were complex [96]. From a historically point of view, the compatibilization of immiscible blend by nanofiller was first reported for carbon black particles dispersed in elastomers [41,42]. Then, Gubbels et al. [75,45] showed that carbon black particles enlarge the composition range in which co-continuity was obtained. If the amount of carbon black is less than 2 wt%, the morphology coarsens significantly but remains co-continuous. Above 2 wt%, for instance at 5 wt% of carbon black the morphology is stabilized. From a mechanism point of view, the increase of the viscosity of the PE phase containing fillers is thought to be responsible for the inhibition of the coalescence. Clarke et al. [83] showed that carbon black has a powerful compatibilizing effect when the particles are present at the interface between natural rubber and nitrile butadiene rubber phases. Regarding silica particles, Liu and Kontopoulou [97] showed that the addition of nanosilica particles into PP/poly(ethylene-*co*-octene) blend decreased the size of the dispersed elastomer phase. Elias et al. [64] and Zhang et al. [98], observed also for PP/PS blends a drastic reduction of the size of the PS phase corresponding to a concentration of hydrophobic fumed silica at the interface (Fig. 11). With the help of viscoelastic analysis (see rheological section), the authors concluded that the stabilization mechanism of PP/PS blend by hydrophilic silica is the reduction of the effective interfacial tension whereas hydrophobic silica acts as a rigid layer preventing the coalescence of PS droplets. Zhang noticed that after passing an optimum morphology, increasing the mixing time results in a late coarsening of the dispersed PS domains accompanied by a redispersion of the silica into the PP matrix rather than at the interface. The compatibilization is thought to be kinetically controlled in that case. However the relatively long mixing time (20 min) are also able to degrade the PP and subsequently modify the viscosity ratio of the blend so that it is difficult to draw unambiguous conclusions from their results.

Recent studies [90,96,99–115] have been reported on layered silicates acting as compatibilizing agents in immiscible polymer blends. The refinement of the morphology may be sometimes very drastic. For example Si et al. and Ray et al. on PC/SAN and PC/PMMA blends respectively, showed that at the concentration of organoclay around 5 wt% the blends normally immiscible depict the characteristics of a "miscible" blend with only one alpha relaxation peak [104–107]. Furthermore, both polymer phases are hardly distinguished in the TEM pictures. However, it is difficult to ascertain whether the blend is miscible at the molecular scale, more probably the small size of the phases and their immobilization by the strong interactions with the solid are the cause of this apparent miscibility. Also, in the case of PC/PMMA blends, transesterification reaction between PC and PMMA chains can be catalyzed by the clay as this

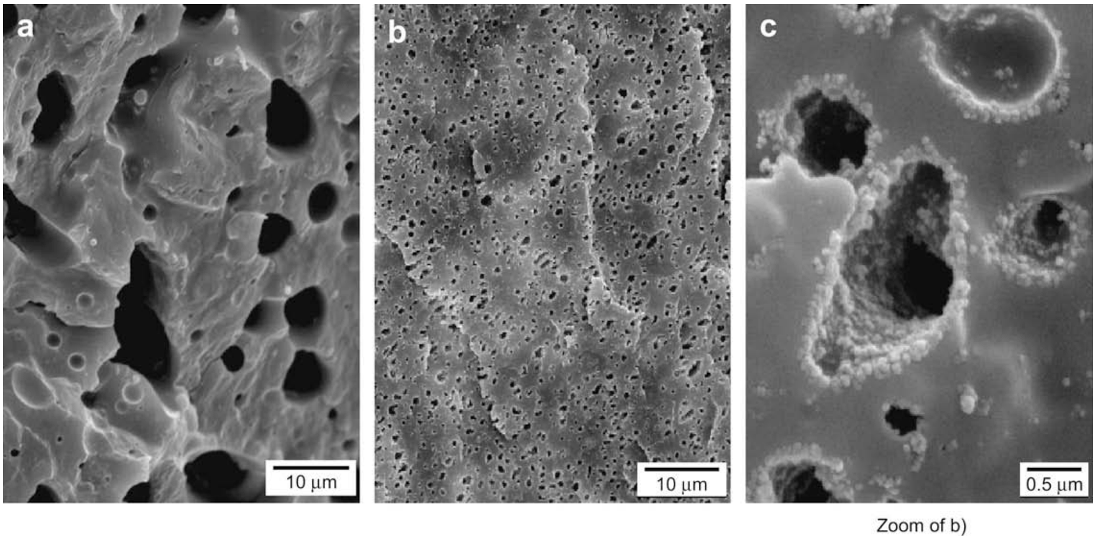

Fig. 11. Morphology of polypropylene/polystyrene 70/30 wt%. The polystyrene has been extracted by a selective solvent. The blend has been prepared by adding the three components simultaneously in the extruder. a) PP/PS blend without silica. b) Blend filled with 3 wt% of hydrophobic silica. c) Zoom of image b) showing silica particles in the PP phase and concentrated at the interface. From [64].

aluminosilicate can produce Lewis or Bronsted sites at high temperatures.

Not only the size but also the shape of the dispersed polymer drops can be altered, especially in the presence of high shape factor particles. Si et al. observed that PMMA preferentially adsorbs at the clay surface so that the particles are dispersed in the PMMA phase and at the interface of the PS/PMMA blends [107]. The size of the PMMA domains is very small (<1 μm) and interestingly, the PMMA domains do not remain rounded like in the pure polymer blend (Fig. 12).

The clay platelets are designing the contour of the drops and they impose the interfacial curvature. The authors hypothesize that clay have to bend to hug the surface of the drop. Thus it exists a minimum size attainable for the dispersed polymer and it is related to the rigidity modulus of the platelets. Si et al. estimate the minimum radius of such drops surrounded by clay layers by expressing the free energy of the system corrected by a factor that accounts for the bending energy of the platelets located at the interface. The radius of the domain that can be formed before it can be destabilized by the difficulty in bending is [107]:

$$r \approx \left(\frac{Eh}{\gamma - \gamma'}\right)^{1/4} l \tag{9}$$

where E is the rigidity modulus, h and l are the thickness and the characteristic length of a platelet, γ and γ' are the interfacial energies between the polymers and when the clay platelets are at the interface respectively. A calculation by taking $\gamma = 2$ mN/m, $E = 1$ GPa and $\gamma' \ll \gamma$ leads to the conclusion that the minimum domain radius will be equal to the characteristic length of a platelet, l.

4.3.2. Mechanisms of compatibilization

Undoubtedly, numerous experimental works evidence the compatibilizing effect of nanofillers on binary polymer blends nevertheless several interpretations are proposed. The work of Ray and co-workers [104–106] summarizes well the questions that arise when trying to identify the mechanisms involved in the refinement of the morphology by nanofillers. Actually, several phenomena can lead to morphology changes: i) a reduction of the interfacial energy, ii) the inhibition of coalescence by the presence of a solid barrier around the minor polymer drops, iii) the changes of the viscosity of the phases due to the uneven distribution of the filler, iv) the immobilization of the dispersed drops (or of the matrix) by the creation of a physical network of particles when the concentration of solid is above the percolation threshold and v) the strong interaction of polymer chains onto the solid particles inducing steric hinderance.

The discrimination and classification of the above potential mechanisms are very difficult due to the lack of models and experimental works with the objective to separate the influential parameters (thermodynamic effects, kinetic effects, particle localization, transfer of particles). For instance, most of the conclusions on the impact of the distribution of the filler inside the biphasic material are drawn from the observation of the final morphology and does not necessarily account for the displacements of the particles during the course of mixing. A second illustration of the difficulties is linked to the viscosity evolution of the phases that may be very complex since related to the local filler concentration and state of agglomeration or exfoliation (that can be time dependent). Despite these complications it is nevertheless possible to extract basic knowledge from the diversity of the publications.

The reduction of the interfacial tension due to the distribution of the filler at the polymer/polymer interface is often cited as a potential explanation for the compatibilization [64,65,104,116]. The interfacial tension change is sometimes calculated with the help of rheology and the reader can refer to the section dedicated to viscoelastic properties. Actually, the interface between the two polymers can be seen as a more complicated interfacial zone with filler/polymer1, filler/polymer 2 and polymer1/polymer2 interfaces. Thus, the definition of an apparent or an effective interfacial tension is more appropriate [18]. The modification of the interfacial tension affects the breakup/colascence equilibrium in favor of the breakup and should lead to smaller drops. In addition the filler can form a rigid shell around the polymer drop, modifying strongly its deformation ability. This is observed in low viscosity emulsions when the total coverage of the interface by interacting solid particles is achieved.

As a second mechanism, many authors agree to assert that the definitive or temporary localization of the nanofiller at the interface of a blend is one of the requisite mechanisms to ensure a reduction of the size of the minor polymer phase. The similarity with liquid emulsions is again highlighted as the particles accumulated at the interface build a solid barrier preventing the fusion of the drops. A schematic description of the mechanism is given in Fig. 13a1 and an example of the possible corresponding morphology is depicted in Fig. 13a2. The nice TEM picture from the study of Hong and co-workers [108] on PBT/PE/clay has been selected to illustrate that mechanism because the embedding of the PE drops by clay platelets appears well but other publications highlight the same phenomenon with other fillers [102,104,108].

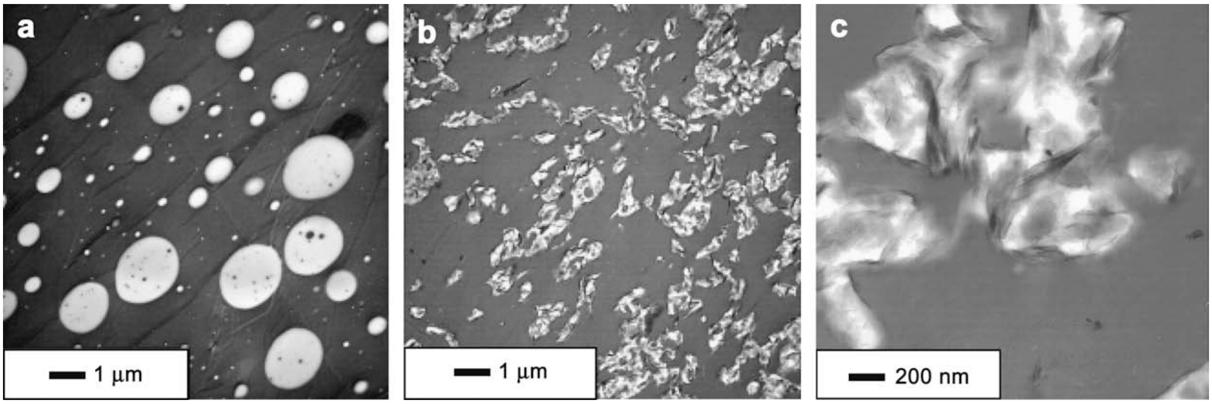

Fig. 12. TEM images of (a) PS/PMMA 27/63, (b) PS/PMMA (27/63)/nanoclay (10 wt%), (c) zoom of (b). All blends are annealed at 190 °C for 14 h. The clay confines into the PMMA phase due to favorable interactions. The presence of the clay stabilizes the morphology. The PMMA droplets (in white) do not retain their rounded shape when they contain clay. From [107] reprinted with permission from ACS.

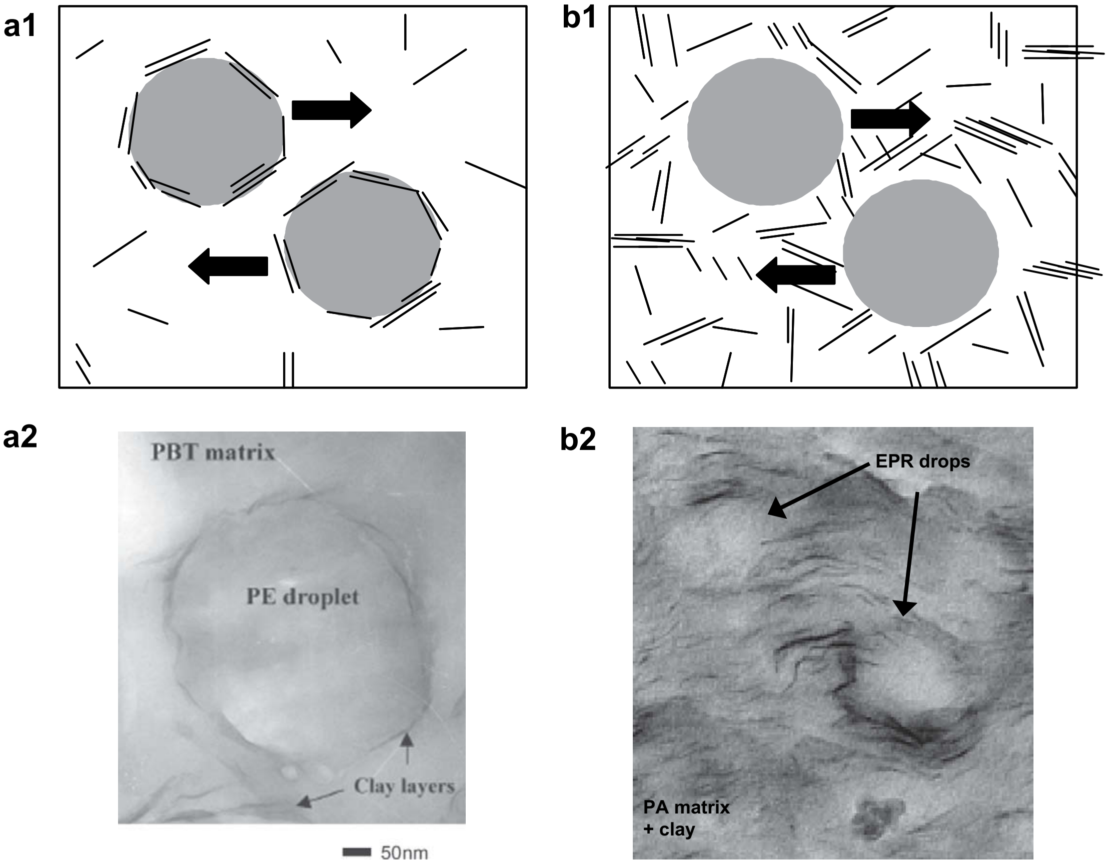

Fig. 13. Two of the possible mechanism explaining coalescence inhibition in polymer blends containing nanofillers (layered silicate type in the illustration). a1) Barrier of particles concentrated at the interface and a2) actual example of the corresponding possible type of morphology extracted from [108]. b1) Particles confined in the matrix acting as obstacles to coalescence and b2) actual example of the corresponding possible type of morphology extracted from [109].

In situations where a polar polymer like polyamide (PA), polyester or maleated olefins is employed for the matrix, the filler distributes in that phase due to favorable polymer–particle interaction. An important reduction of the drop size is nevertheless sometimes reported [90,101,109,115,117]. If the filler has a high aspect ratio (clay for instance) it may be trapped in the matrix film between two colliding drops and slow down coalescence. This phenomenon is illustrated in Fig. 13b1 and b2 with an example of the morphology obtained for a PA6/poly(ethylene-*co*-propylene) (EPR) where it appears that two drops will hardly fuse [109]. On the other hand with a lower aspect ratio filler, Liu et al. pointed out that silica was distributed exclusively in the PP/PP-*g*-MA major phase of their PP/PP-*g*-MA/poly(ethylene-*co*-octene) (POE) blend and only a slight improvement of the morphology was pointed out [97]. In that case, an increase of the viscosity of the matrix may be the cause of the morphology change since silica does not constitute sufficient blockage. With the same type of blend but filled with organically modified montmorillonite Lee et al. obtained an impressive reduction of the size of the POE phase to 0.44 μm depicted in Fig. 14 [117]. It is to be noticed that the montmorillonite was supposed to distribute into the PP/PP-*g*-MA matrix phase despite no clear evidence of this point was presented. Thus it seems that the presence of particles inside the matrix may inhibit coalescence provided that no other factor dominates.

When rheological constrains are encountered, coalescence is not inhibited. Wu et al. [118] showed that the presence of clay does not prevent the coalescence of the PPS phase, in PPS/PBT blend with the clay mainly located in the continuous PBT phase. The elasticity and viscosity ratio, which considerably changes with the preferential location of clay in PBT phase, combined with shear history actually control the morphological evolution. Such effect was also reported by Zhang et al. [119] for PP/liquid crystal blend with 5% of hydrophilic fumed silica as the silica is located in the dispersed phase (80% PP/20% liquid crystal).

Coalescence should not be the only factor considered. The accumulation of solid particles inside the polymer drops may cause a shift in the breakup/coalescence equilibrium. The viscosity of the drop may rise to a point where breakup is inhibited or even suppressed if the concentration of particles is such that they form a rigid network that immobilizes it. In a PE/PBT blend in which PBT is the minor phase and the proportion of clay is increased, the platelets show the tendency to reside in the PBT phase. Hong et al. observed that the size of the dispersed domains increases [108]. They hypothesized that the viscosity rise of the drops is such that the breakup process is made difficult.

Finally, if we refer to the compatibilization by block copolymers, a mechanism of coalescence inhibition by steric hinderance may be imagined with fillers provided that the macromolecules are strongly adsorbed to the filler surface. Fig. 15 illustrates how the interface between two polymers may be stabilized by clay platelets depending on the strength of interaction [114].

In the situation depicted in Fig. 15a the silicate is the coupling species between the polymers and a layer of polymer A/silicate/polymer B is present at the interface playing a role similar to a block copolymer. This picture although very schematic has the advantage of visualizing different cases but experimental evidence of the type and amount of coupling is very difficult to obtain.

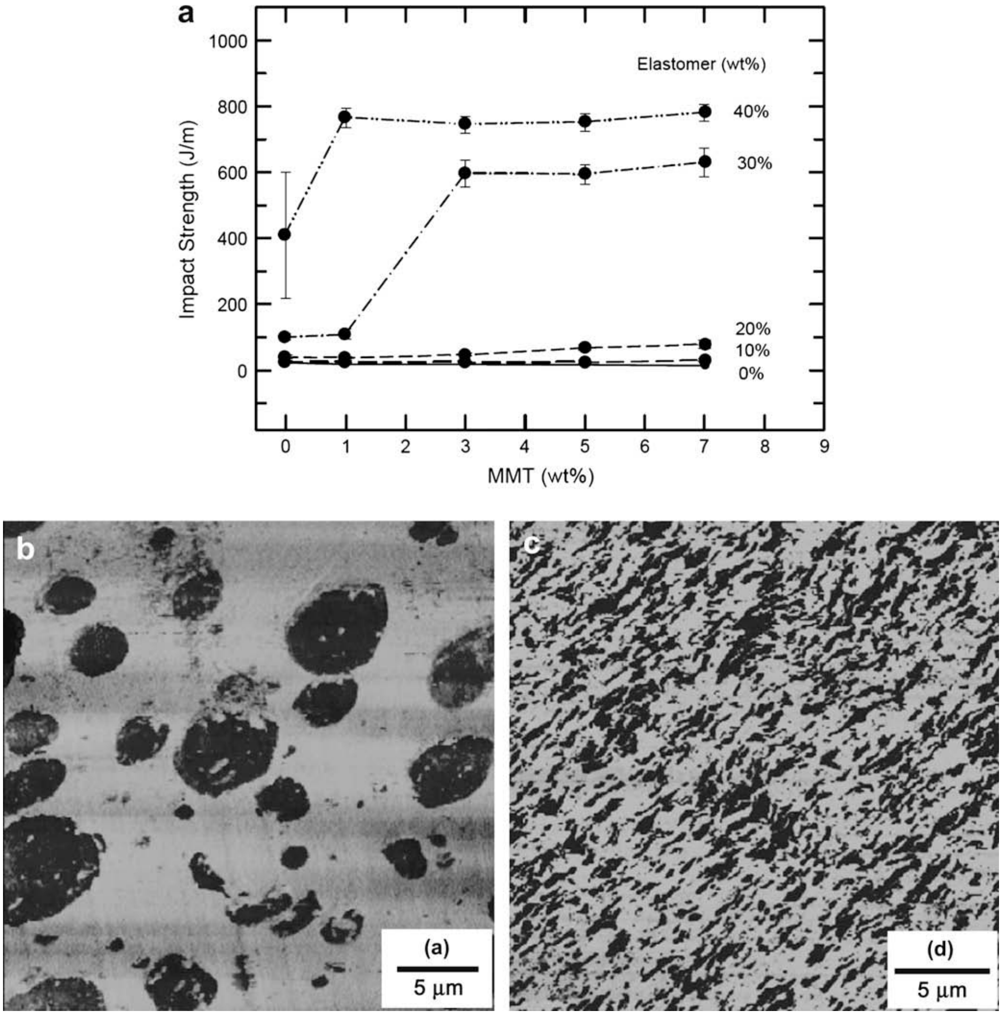

Fig. 14. (a) Notched impact strength of the PP/PP-*g*-MA/poly(ethylene-*co*-octene)/montmorillonite nanocomposites with variable proportion of POE elastomer and organoclay. (b) and (c) AFM images of the blend containing 30 wt% of POE elastomer and 0 wt% and 6.8 wt% respectively of montmorillonite showing the impressive change of the morphology induced by the presence of the clay inside the PP/PP-*g*-MA matrix. From [117].

4.3.3. Stability of the morphology

The stability of the morphology is another important aspect in the development of new materials. Polymer blends are produced by twin-screw extrusion which is an efficient mixing process. Nevertheless, the stability of the morphology is required to ensure constant properties that will not be deteriorated after a second extrusion or injection molding step. This stability is not studied very often. Most of the time, the experiment consists in annealing the samples and observing the morphology after several hours at high temperature. The example of the PE/PS 45/55 co-continuous blends of Gubbels et al. can be again cited [44]. The effect of annealing the materials by compression molding at different times and temperatures is emphasized. If the amount of carbon black is less than 2 wt%, the morphology coarsens significantly but remains co-continuous. Above 2 wt%, for instance at 5 wt% of carbon black the morphology is stabilized. When the conductive particles are concentrated at the interface an additional effect of the annealing time is pointed out [45]. Annealing results in a decrease of the percolation threshold. The interpretation is the following: in the molten state and in the absence of shear the interfacial area of the blend spontaneously decreases, that is the tortuosity of the PE phase decreases. Since the particles do not leave the interface, the consequence is a local increase of the particle concentration which is in favor of a further decrease of the percolation threshold. With that strategy only 0.4 wt% of carbon in a PE/PS 45/55 was enough to obtain conductivity of the material with a resistivity close to

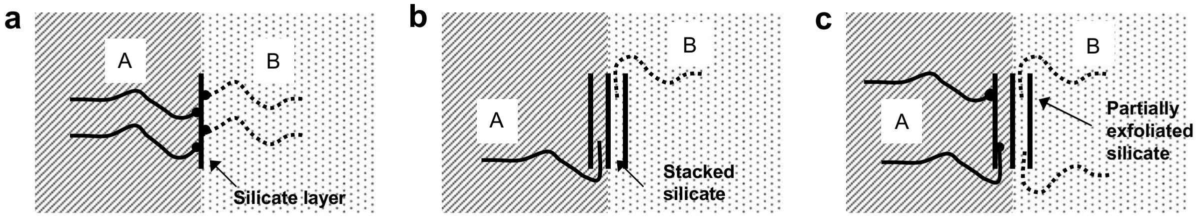

Fig. 15. Hypothesis on the compatibilization mechanisms by layered silicates. (a) Polymers A and B have strong interaction with the silicate, (b) both polymers have weak interaction with the silicate, (c) polymer A has strong and polymer B weak interaction with the silicate. From [114] reprinted with permission of John Wiley and sons.

100 Ω cm. The study of Si et al. demonstrated that the stability against annealing was greatly enhanced in the presence of organoclay for two types of blends: PS/PMMA and PC/SAN (Fig. 12) [107].

Obviously, quiescent annealing does not reflect the actual conditions of a processing under shear but not much data are reported for re-processing to our knowledge.

4.3.4. Mechanical properties

The other critical point in the compatibilization of immiscible polymer blends is the amelioration of the ultimate mechanical properties that is evidenced when the compatibilizing agent is adequately selected. It is not such a surprise that the modulus is increased by the addition of high rigidity fillers but stress and strain at break are much more relevant criteria to consider than the modulus since they are affected by the interfacial adhesion. By contrast with copolymers nanofillers do not considerably improve the tensile mechanical properties of filled blends. Generally, the elongation and stress at break are often reduced as well as impact properties [97,98,104,117]. Nevertheless, Yang et al. [120] showed that the formation of filler-network structure lead to super toughened PP ternary composite with the Izod impact strength 2–3 times higher than PP/EPDM binary blend and 15–20 times higher than pure PP. On the other hand, Kelnar et al. reported that the localization of two different types of clays at the interfacial area and in the polyamide phase of a polyamide/elastomer blend leads to an improvement of the toughening effect by the formation of core-shell particles [109]. They obtained a better result by pre-blending the less polar clay with the elastomer prior to the addition of the polyamide. Acharya et al. [121] reported a considerable increase in thermal properties of EPDM/EVA/clays.

With PP/PP-*g*-MA/poly(ethylene-*co*-octene)/montmorillonite blend Lee et al. observed a super-toughness behavior only for materials containing more than 20 wt% of elastomer [117]. These good mechanical properties were explained by the morphological change in the presence of the filler that reduced the size of the elastomer domains to less than 1 μm (Fig. 14). On the other hand the elongation at break decreases for all the nanocomposites.

In the domain of strain recovery, a morphology effect is noticed with PP/EPDM blends filled with nanosilica. The presence of the particles improves the final strain recovery of the elastomer and induces a double step recovery profile attributed to the presence of large aggregates inside the elastomeric phase [122].

The fact that less indications are found on the literature on whether or not nanofillers are improving high deformation mechanical properties is certainly the indication that results are contradictory. When compatibilizing copolymers are used, their blocks entangle with the corresponding miscible polymer chains so that covalent bond ensure the cohesion of the interface. With fillers this is not the case except if strong interactions exit between the polymers and the surface of the filler.

4.3.5. Viscoelastic properties

From an experimental point of view, the linear viscoelastic properties of nanocomposites are known to be extremely sensitive to the structure, particle size, shape and surface characteristics of the filler [123]. Consequently, linear rheology is one way generally used to assess the state of dispersion of nanocomposites directly in the melt state. Regarding immiscible polymer blends, Vermant et al. [124] reported first by rheology the effect of nanometer sized silica in coalescence of model PDMS/PIB blends. Well-defined flow histories followed by frequency sweep were used to interpret the influence of silica on blend morphology. The authors clearly demonstrated that the change in the properties of the interface, by silica adsorption are responsible for the suppression or delay of the coalescence. However silica particles prevent coalescence in blends provided that the PIB phase is the minor one and the PDMS the matrix. On the other hand, Thareja and Velankar [23] observed for the same system a gel-like behavior. Three causes of this particular behavior could be relevant: i) particle–particle interaction, ii) drop–drop hydrodynamic interaction and iii) particle-induced clustering (droplet bridging via silica particles). However the authors could not conclude to a clear analysis due to the aggregated structure (fractal behavior) of the fumed silica. Furthermore, they did not fully agree with the conclusion of Vermant et al. as some apparent discrepancies have been evidenced between their results. This debate between Vermant et al. and Thareja et al. has been carried on in their respective recent papers [125,126]. Finally, the mechanism of particle bridging can really induce a gel-like behavior. However, particle bridging is not believed to be the dominant mechanism for stabilization of the blend morphology by inorganic particles.

From an experimental point of view, the shape relaxation of the dispersed polymer phase can be usefully evidenced from the variation of $\eta''(\omega)$. For instance, Fig. 16 shows in the domain of low frequencies the second domain of relaxation corresponding to the relaxation of polymer droplets. Furthermore, Fig. 16 shows also that the addition of silica particles induces a modification of the second domain of relaxation which reflects a change in the droplet shape relaxation. A shift of the relaxation time and modification of the shape of the relaxation peak are observed.

From a quantitative point of view, Palierne [127] and Bousmina [128] developed a model able to predict the linear viscoelastic behavior of emulsions, taking into account the interfacial tension between the components, the size of the dispersed phase and the viscoelastic property of both components. However, the situation of filled polymer blends is complicated by the presence of the nanofiller. Vermant et al. argued that fitting the Palierne model to the experimental data turned out to be difficult even when introducing an additional fit parameter to take interfacial elasticity into account [124]. Then, Vermant et al. preferred to use the ratio R/γ_{12} (interfacial elasticity) to avoid any ambiguity concerning the interfacial tension. Actually, R/γ_{12} was calculated by expressing the drop relaxation time τ according to the following equation derived from the Palierne model:

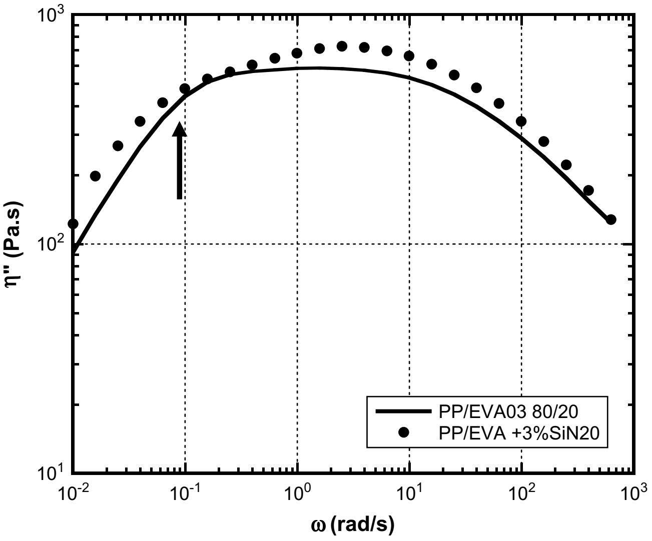

Fig. 16. Frequency dependence of η'' for the PP/EVA (80/20) blend filled with 3 wt% of hydrophilic silica particles. The silica particles have been simultaneously dispersed in PP/EVA blend during mixing. The arrow indicates the relaxation time of the EVA droplets. From [65].

$$\tau = \frac{R\eta}{4\gamma_{12}} \frac{(19p+16)(2p+3-2\phi(p-1))}{10(p+1)-2\phi(5p+2)} \tag{10}$$

In order to overcome this difficulty, we addressed in a previous work [65] an improved route to calculate the ratio γ_{12}/R_v using the rheological behavior of immiscible blend filled with solid particles. The ratio γ_{12}/R_v is accessible after isolating the droplet contribution to the complex relaxation modulus. Indeed, the Palierne model can be divided in two contributions according to the following form:

$$G^*_{\text{Palierne}} = G^*_{\text{Composition}} + G^*_{\text{droplet}} \tag{11}$$

where $G^*_{\text{Composition}}$ is the complex shear moduli of the blend without any interfacial effects. The Kerner model [129] is able to predict precisely such behavior. Actually, Kerner model corresponds to the Palierne model with interfacial tension set to zero.

G^*_{droplet} captures the interfacial effects and specially the extra-elasticity brought by the droplet deformability. Furthermore, it is easily shown that the storage part of the complex shear modulus G' for a blend of two viscoelastic fluids can be expressed as follows:

$$\begin{aligned} G'_{\text{Palieme}}\left(\gamma_{12}, G^*_{\text{m}}, G^*_{\text{d}}\right) &= G'_{\text{Palierne}}\left(0, G^*_{\text{m}}, G^*_{\text{d}}\right) \\ &\quad + G'_{\text{Palierne}}(\gamma_{12}, \eta_{\text{m}}, \eta_{\text{d}}) \\ &= G'_{\text{Kerner}} + G'_{\text{Kerner}}(\gamma_{12}, \eta_{\text{m}}, \eta_{\text{d}}) \end{aligned} \tag{12}$$

where G^*_{m}, G^*_{d}, are respectively the complex shear moduli of the matrix and the dispersed phase, $\eta_{\text{m}}, \eta_{\text{d}}$ are respectively the Newtonian viscosity of the matrix and that of the dispersed phase. In the previous equation, only the second term depends on the interfacial tension. This corresponds to the droplet contribution G^*_{droplet}. This part can be easily isolated. The main idea of the method is to reveal the contribution of the relaxation of the droplets which depends on the interfacial tension γ_{12} by subtracting the composition effects to the experimental data of G^*. This implies obviously that Kerner's model correctly describes the polymer blend complex shear modulus. This is checked in the high frequencies zone for which the effect of droplet relaxation and then interfacial tension is negligible (Fig. 17).

According to this method, the effective interfacial tension of PP/EVA blend was derived [65] from the experimental measurement of R_v and fitting the experimental curves of the complex shear modulus (Fig. 17). The results show that adding silica in the blends tends to decrease significantly the effective interfacial tension from 0.75 mN/m to 0.25 mN/m whatever the nature of the surface of the silica, hydrophobic or hydrophilic.

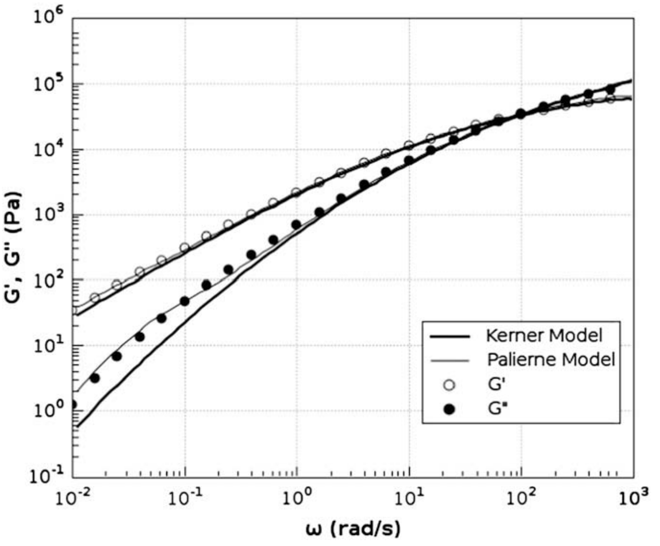

Fig. 17. Modeling of the viscoelastic behavior of PP/EVA 80/20 with 3 wt% silica particles. $T = 200$ °C. The thick line represents the prediction from Kerners' model. The thin line corresponds to the Paliernes' model with $\gamma_{12}/R = 550$ Pa [65].

Hong et al. [116] calculated the interfacial tension of a PBT/PE/organoclay blend from the measurement of the extensional force in molten conditions. Actually this method is based on the work of Levitt et al. [130] who suggested a direct method based on a uniaxial extension experiment to measure the interfacial tension in blend systems. The measured force is expressed from the contribution of each polymer components and of the interfacial tension:

$$F_{\text{blend}} = \phi_1 F_1 + \phi_2 F_2 + \gamma_{12} D_{\text{avg}} N_1 \tag{13}$$

F_i (with $i = 1, 2$) is the force of component 1 and 2 and $\gamma_{12} D_{\text{avg}} N_1$ is the interfacial force. D_{avg} is the average volume diameter of a droplet (component 1 as minor phase). However, the predictions are limited to the early stage of extension. From this method, Hong et al. measured a reduction of interfacial tension from 55.6 to 1.40 mN/m when 1% of organoclay was added in PBT/PE blend [116].

From quantitative analysis of rheological experiments, it can be concluded that the reduction of the interfacial tension, more rigorously effective interfacial tension, is an effective mechanism of blend compatibilization as was stated in a previous section. These results are in agreement with results obtained in liquid emulsions.

5. Conclusion

The objectives of this review was to consider the reasons for the uneven distribution of nanofillers in polymer blends and identify the parameters with which one can play to produce a desired morphology.

- At the thermodynamic equilibrium, nanofiller distribution in immiscible polymer blends is governed by the minimization of the overall free energy generated by the existence of three types of interfaces: polymer 1/polymer 2, filler/polymer 1 and filler/polymer 2 interfaces. The nanoparticles may distribute unevenly among the phases or possibly form a layer at the fluid–fluid interface that consequently reduces the shared area between the polymeric phases. The segregation is linked to the wettability of the particles by the polymers and it may possibly be predicted. Unfortunately, the lack of reliable techniques to determine accurately the filler–polymer interfacial energy is a real issue and more particularly at high temperature. Therefore, polymer–filler interfacial energy is most often estimated from the surface tension of the fillers and this is probably one of the reasons why discrepancies are sometimes observed between theory and experiments.
- Moreover, in viscous systems like polymers, the equilibrium distribution of the filler is attained after a period of time (estimated to several minutes) during which solid particles move inside the blend before reaching their position of better stability. Hence if the molten blend is quenched before an equilibrium is attained, the particles' localization may be different from that assumed by the theory. One can take advantage of this kinetic control to produce non-equilibrium morphologies without the help of expensive and toxic filler surface treatments. The kinetic effect is strongly influenced by the sequence of addition of the components of the blend, by the viscosity evolution of the phases and by the competitive adsorption/desorption of the two polymers. The three factors

are strongly coupled so that very few studies succeed in separating and analyzing correctly their respective qualitative and quantitative influences. Obviously the design of model experiments is a necessity to get a comprehensive overview of the kinetic effects.

- The mechanisms of solid particles migration and the possible existence of a balance between thermodynamically driven particle localization, adsorption/desorption kinetics and the mechanical pull out of the macromolecular chains by shear forces remains to be studied methodically. This opens a large field for comprehensive studies.
- In a large majority of cases, polymer blends filled with nanoparticles show a better compatibility in terms of morphology size than pure blends. Actually, the morphology is finer and more stable against annealing likewise when block copolymers are added to the blend. Among the different potential mechanisms of compatibilization, a decisive one is the temporary or permanent accumulation of the filler at the blend interface. A solid barrier is formed that inhibit or prevents drop coalescence. In addition, the concentration of solid at the interface lowers the apparent interfacial tension as proved by our studies based on the Palierne model developments to nanocomposite polymer blends. Less marked improvement is observed when the particles distribute exclusively inside the minor phase or the matrix. While the improvement of the quality of the morphology is proved, its stability against further processing is not and experiments on that particular point are needed.
- Finally, the benefits of introducing nanofillers on the ultimate mechanical properties of the blends are not always demonstrated. The compatibilization with nanoparticles seems much more difficult to optimize than that induced by block copolymers. The fact that copolymers are entangled with the respective polymer phases while polymer/filler interactions constitute often weaker links is probably one of the reasons. In the domain of more specific properties like antistatic or conductive characteristics, the control of the uneven distribution of particles, and more particularly at the interface, was successfully used to minimize the concentration of conductive fillers needed to induce electrical conductivity (concept of double percolation). Finally, as a perspective, the control of the distribution of “reactive fillers” could be imagined to induce a chemical reaction, as crosslinking for instance, directed at the interface between polymers.

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